

## XPS STUDY OF CATALYSTS AND CATALYST IMPREGNATED COAL

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### INTRODUCTION

The highly dispersed forms of certain catalysts are believed to be very active in the conversion of coal to liquids via direct liquefaction.<sup>1-3</sup> A catalyst with a higher specific surface area and fine particulate size can be utilized at small concentrations to achieve better performance in terms of overall coal conversion and selectivity to lighter products (oils) in direct coal liquefaction.<sup>4</sup>

X-ray photoelectron spectroscopy (XPS) has been used to study the surface characteristics of six catalysts and a catalyst impregnated Illinois #6 coal. This technique provides the surface elemental distribution and chemical information about the outermost 3-4 nm of the exposed solid surface. This characterization has shown that the concentration of elements at the outermost layer measured by XPS is different from that in the bulk determined by chemical analysis. The oxygen concentration was enriched in the surface regions of all the samples. The oxidation states of these elements were generally identified.

XPS depth profiling studies also have been carried out to determine if there are any differences in the distribution of the major components in catalyst II ( $\text{Mo/FeOOH/SO}_4^{2-}$ ) and catalyst I ( $\text{FeOOH/SO}_4^{2-}$ ) impregnated Illinois #6 coal. A systematic trend towards lower weight concentrations of both oxygen and sulfur was observed for both samples as the sputtering time increased (i.e. when going from surface to the bulk).

### EXPERIMENTAL

Six catalysts and catalyst I ( $\text{FeOOH/SO}_4^{2-}$ ) impregnated Illinois #6 coal were investigated in the surface characterization studies. These samples were obtained from the Univ. of Pittsburgh<sup>5</sup> and are shown in Table I. The powdered samples were examined in their as-received form and their particle sizes were less than -100 mesh.

The powdered samples were mounted on the spectrometer probe tip by means of double-sided adhesive Scotch insulating tape. The samples were pressed with the aid of a metal spatula and the excess that had not adhered was tapped off. To exclude the possibility of recording contaminants associated with the tape, the tape was also analyzed separately. It was found that the constituents of tape were not detected by XPS, and that the photoionization signals are characteristic of the catalyst and coal samples alone.

The samples were examined by XPS on a Kratos XSAM 800 spectrometer using Mg K $\alpha$  (1253.6 eV) radiation. The spectrometer was run in fixed retarding ratio (FRR) mode at a pass energy of 13 kV and 15 mA. Under these conditions, the full width at half maximum (FWHM) of the Ag (3d<sub>5/2</sub>) peak is  $\approx 1.1$  eV. Spectra were recorded at  $< 5 \times 10^{-7}$  torr.

Radiation damage to the sample from long-term exposure to the X-ray beam was not observed. All binding energies were referred to carbon (1s) at 285 eV to compensate for

sample charging. Elemental concentrations were obtained from peak areas and corrected for atomic sensitivity factors.

The peak was deconvoluted using a peak synthesis procedure which employed a Gaussian line shape at fixed binding energies determined from model compound studies.<sup>6</sup> The data system permitted the intensity of the components and their FWHM to be varied in order to obtain the best fit between the experimental and the synthesized spectra.

Ar<sup>+</sup> sputtering of the powdered sample was carried out with the Ar<sup>+</sup> gun operating at 3.5 kV (estimated etching rate of ca. 20 Å/min, as determined from a SiO<sub>2</sub> standard film). Each charge compensation was referred to the C 1s peak at 285 eV.

## RESULTS AND DISCUSSIONS

### Surface Compositions

The XPS spectra showed a distinct peak for major elements, oxygen, iron, and tin, as well as the minor component, sulfur, in each catalyst sample. The C 1s peak was observed in all catalysts and can be ascribed to carbon contamination. Cl 2p was only observed in the tin oxide catalyst (III). This occurs because chlorine was introduced as SnCl<sub>4</sub>·5H<sub>2</sub>O in the starting materials that were used for the preparation of the tin oxide catalysts. This excess chlorine was left at the surface after sample preparation. The quantitative analysis results are shown in Table 2.

To determine the oxidation states of Fe, Mo, and Sn, narrow survey scans were carried out. The binding energies of the Fe 2p, Mo 3d and Sn 3d levels showed the expected values for the most stable oxidation states of these elements. Multiple splitting was observed in the transition elements, such as Fe and Mo. Figures 1a and b show the results for Fe 2p and Mo 3d, respectively. This is the result of spin interaction between an unpaired electron from the photoionization process and other unpaired electrons present in the system. The point of real interest is that the separation between the two peaks varies depending upon the environment of the atom concerned. In Fig. 1a, the Fe 2p peak shows the  $13.6 \pm 0.05$  eV splitting between the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> peaks. This was observed in all iron oxide containing catalysts. The observed splitting corresponds well with the Fe 2p peaks of Fe<sub>2</sub>O<sub>3</sub> and/or FeOOH (Goethite) in model compound studies.<sup>6</sup> The Fe compound shown in the surface of the catalyst samples can thus be ascribed to either Fe<sub>2</sub>O<sub>3</sub> or FeOOH.

Mo 3d showed the 3.2 eV splitting between the 3d<sub>3/2</sub> and 3d<sub>5/2</sub> peaks in the catalyst II, IV, and V samples. Molybdate (MoO<sub>4</sub><sup>2-</sup>) was used as a starting material in the preparation of these catalysts. This anion is readily oxidized at the surface and produces the stable oxidation state MoO<sub>3</sub> at the catalyst surface. Sn 3d also showed the multiple splitting of 8.45 eV. This can be ascribed to SnO<sub>2</sub> and is shown in Fig. 1c. Emphasis has been focused on the S 2p peaks of raw coal samples in earlier reports.<sup>7</sup> It was shown that the S 2p peak always displays two photolines with a separation of 5.6 eV in raw coal samples. However, the XPS spectrum of S 2p in the catalyst samples showed only one S 2p peak at 168.8 eV, corresponding to SO<sub>4</sub><sup>2-</sup>. This result is shown in Fig. 1d where a catalyst spectrum is compared with that of catalyst impregnated coal. In the upper spectrum, the peak at 164 eV can be ascribed to sulfide in the coal.

From the above results, it was concluded that all major elements showed the most stable oxidation states at the surface of all catalysts and catalyst impregnated coal samples.

## Depth Profile Studies

In order to show if there is any difference in the distribution of the elements and chemical changes between the surface and bulk, the samples have been analyzed by combining  $\text{Ar}^+$  sputtering with XPS measurements. Due to the edge effect associated with the unetched sample surface, the depth profiles for materials in powder form were difficult to obtain. Preferred areal sputtering was carried out to reduce this effect. Although different features such as preferential sputtering, atomic mixing, particle size effects, etc., can effect the etching profiles, sputtering was performed in the present studies for comparative purposes on samples where such effects were expected to be very similar.

Figures 2a and b show depth concentration profiles for the most abundant elements in catalyst I and catalyst I impregnated Illinois #6 coal samples, respectively. A systematic trend towards lower weight concentrations of both oxygen and sulfur was observed for both samples as sputtering time increased. A relatively high oxygen concentration was determined initially at the surface by XPS before etching, but a sharp drop in oxygen concentration was subsequently observed as shown in Fig. 2a. This surface enrichment of oxygen can be ascribed to air oxidation and the oxidized layer thickness was estimated to be 40-50 Å. In Fig. 2a, Fe shows an enrichment as the etching proceeds from the surface to the bulk of catalyst I. This was also observed in catalyst II. From these results, which show a decrease in oxygen and an increase in iron concentrations with increased etching, it can be concluded that the surface iron particles are covered with an oxide layer. However, no change was observed in the iron concentration in the case of the catalyst impregnated coal sample shown in Fig. 2b. It can thus be concluded that the iron particles, in catalyst I impregnated Illinois #6 coal, are encapsulated by organic materials from the coal.

Chemical state changes for sulfur were observed as the etching proceeded in both samples. The surface sulfur showed a binding energy of 168.8 eV, indicating sulfate ( $\text{SO}_4^{2-}$ ) and no peaks were observed in the sulfide region (164 eV) in the case of the catalyst I sample. As sputtering time increased, however, the sulfate peak decreased and finally disappeared. A sulfide or elemental sulfur peak was then observed. These results are shown in Figs. 3a and b. This can be ascribed to the removal of oxidized sulfur at the surface by the etching procedure. No chemical state changes were observed for Fe and Mo states as a result of etching.

## SUMMARY AND CONCLUSIONS

It is apparent from this study that XPS can be used to obtain surface chemistry information and elemental identifications on the exposed solid surface. The major elements showed the most stable oxidation states. Sputtering with  $\text{Ar}^+$  is a useful tool in determining depth concentration profiles along the outermost sample surfaces. However, in the case of chemical state changes during etching procedures, the interpretations tend to be inconclusive, unless extensive, time-consuming data accumulation can be performed.

## ACKNOWLEDGEMENT

We gratefully acknowledge financial support from the Consortium for Fossil Fuel Liquefaction Science, Univ. of Kentucky under Dept. of Energy Contract no. DE-FC22-90 PC 90029. We also thank Dr. G.P. Huffman for his interest in this work.

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**Table 1. Summary of Materials**

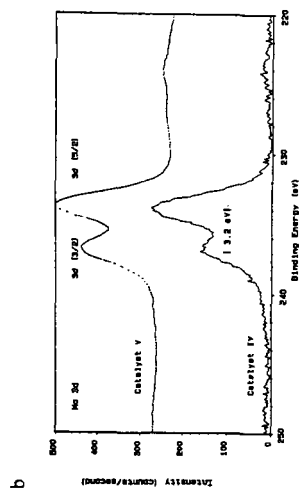
Catalyst	Symbol	Elemental Analysis
FeOOH/ $\text{SO}_4^{2-}$	I	3.0 wt% Sulfur
Mo/FeOOH/ $\text{SO}_4^{2-}$	II	1.0 wt% Mo and 2.0 wt% Sulfur
FeOOH/SnO(OH) <sub>2</sub> / $\text{SO}_4^{2-}$	III	
Mo/ $\text{Fe}_2\text{O}_3$ / $\text{SO}_4^{2-}$	IV	0.5 wt% Mo and 1.3 wt% Sulfur
$\text{Fe}_2\text{O}_3$ / $\text{MoO}_4^{2-}$	V	2.0 wt% Mo
SnO <sub>2</sub> / $\text{SO}_4^{2-}$	VI	
FeOOH/ $\text{SO}_4^{2-}$ on Ill. #6		10.0 wt% Fe and 2.0 wt% Sulfur

**Table 2. Bulk and Surface Concentrations (wt%) for Catalysts**

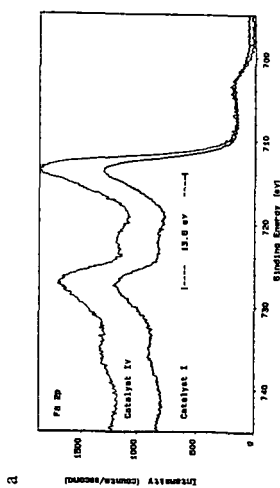
	I		II		IV		V		III	VI
Element	Bulk	XPS	Bulk	XPS	Bulk	XPS	Bulk	XPS	XPS	XPS
Fe	57.85	40.79	59.12	40.43	68.87	40.71	67.61	34.69	27.09	
O	34.15	52.24	37.88	48.65	31.34	46.22	30.09	39.97	30.55	19.07
S	3.00	6.97	2.00	4.51	1.30	6.34			0.46	2.05
Mo			1.00	6.40	0.50	6.74	2.00	25.94		
Sn									41.89	78.88

FeOOH/  $\text{SO}_4^{2-}$  on Ill. #6 --- C:43.46, O:38.54, Fe:6.67, S:1.87, Al:3.48, Si:3.97

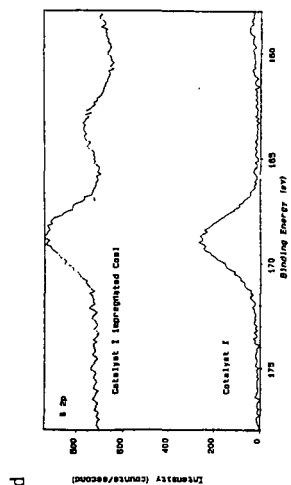
Raw Coal (Illinois #6) ----- C:66.58, O:22.53, S:1.52, Al:3.99, Si 4.3



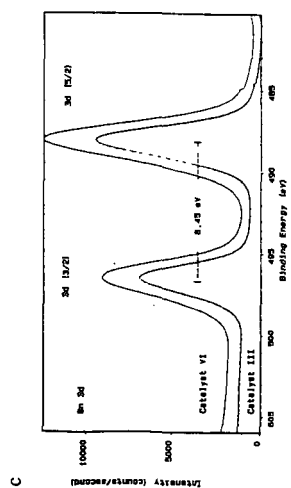
b



c



d



e

Figure 1. Typical XPS narrow scan spectra for (a) Fe 2p for catalysts I & IV, (b) Mo 3d for IV & V, (c) Sn 3d for III & VI, and (d) S 2p for catalyst I and catalyst I impregnated on Illinois #6 coal

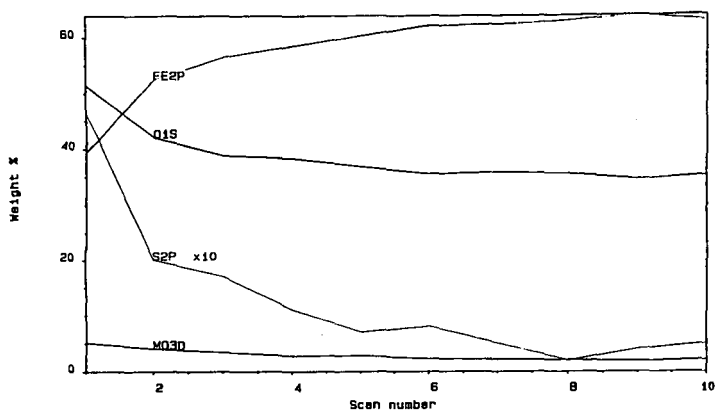


Figure 2-a. XPS depth profile of Catalyst I

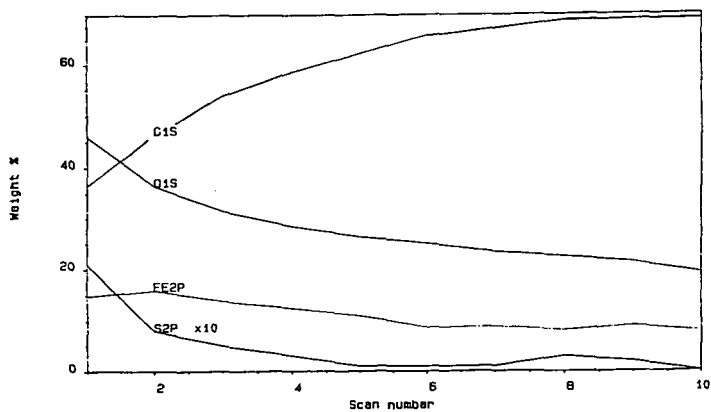


Figure 2-b. XPS depth profile of Catalyst I impregnated on Illinois #6 coal

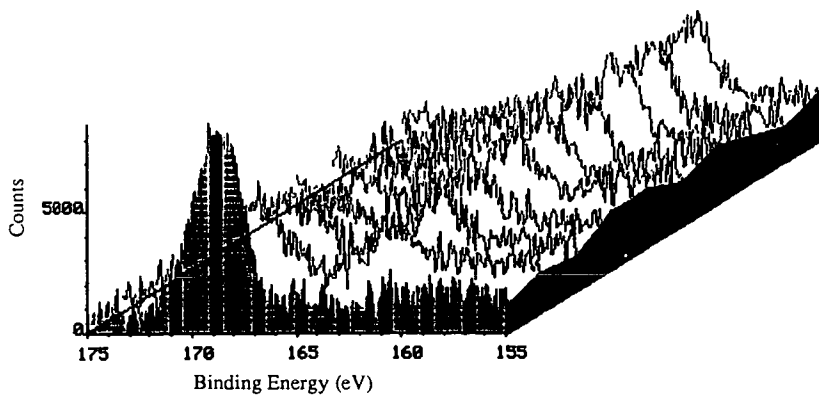


Figure 3-a. XPS depth profile of Sulfur in Catalyst II

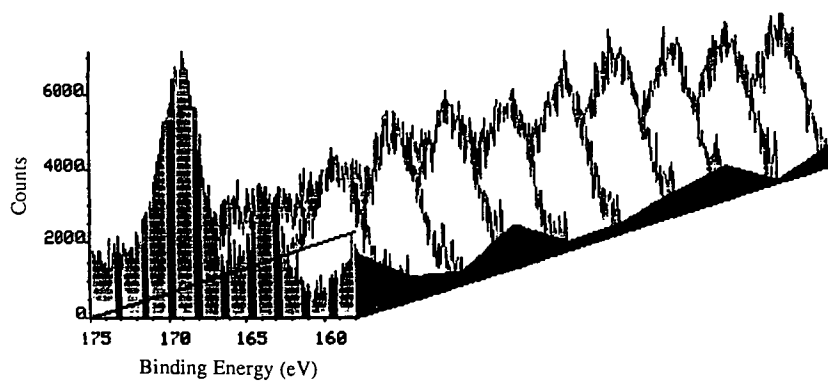


Figure 3-b. XPS depth profile of Sulfur in Catalyst I impregnated Illinois #6 coal